(12) UK Patent Application (19) GB (11) 2 033 425 A

(21) Application No 7843108
(22) Date of filing 3 Nov 1978
(43) Application published 21 May 1980
(51) INT CL³ C22C 5/08 9/00
(52) Domestic classification C7A B230 B23X B23Y B279 B289 B309 B319 B320 B32X B32Y B348 B369 B389 B399 B419 B439 B440 B449 B44Y B451 B453 B455 B457 B459 B45X B489 B519 B539 B549 B559 B610 B611 B613 B616 B619 B621 B624 B627 B62X B630 B635 B636 B63Y B661 B663 B665 B667 B669 B66X B670
(56) Documents cited GB 442773.
(58) Field of search C7A
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(54) Silver-copper-germanium Alloys Having High Oxidation Resistant Melts

(57) A silver-copper-germanium base alloy is disclosed consisting by weight of 40 to 85% silver, 15 to 60% copper and 0.1 to 10% germanium.

Optionally, up to 15% by weight of the base alloy may be replaced with tin and up to 10% by weight of at least one of gold, palladium and platinum. The presence of germanium in the alloy virtually eliminates oxidation of the melt during the melting and casting of the alloy and thereby also improves resistance to tarnishing when the alloy is used in an oral environment.

This print embodies corrections made under Section 117(1) of the Patents Act 1977.

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SPECIFICATION

Silver-Copper-Germanium Alloys Having High Oxidation Resistant Melts

The present invention relates to alloys which are composed essentially of silver, copper, and germanium, such combination hereinafter referred to as the base all y, and optionally to the base alloys containing tin and varying amounts of precious metals, as for example, gold, palladium and platinum.

Conventional cast r wrought dental alloys, such as those used for inlays, crowns, bridges, and partial dentures, usually contain ver 45% by weight of at least on f th precious metals: gold, palladium and platinum, which impart to the alloy the properties of high toughness, the ability to be easily fabricated and good corrosion resistance. Because of the high precious metal content in these types of alloys, the costs of preparing these alloys due to the present high cost of the metals is becoming exorbitant; thus one of the objects of the present invention is to provide new compositions of dental alloys which contain either no precious metals or which have a much lower amount of the precious metals than conventional alloys.

The term "precious metal" as used herein is applicable to gold, palladium and platinum only or to combinations of two or all of these metals.

The base alloys of silver-copper-germanium of this present concept exhibit excellent casting properties as well as ease of fabricating, a hardness that increases with solidification rate and virtually no tendency to oxidation in the liquid state. The base alloys of the present invention have been found to generally have fair corrosion resistance and properties which are desirable for some types of cast alloys employed in dentistry.

I have found that the addition of small to moderate amounts of germanium to silver-copper alloys to produce the present base alloy virtually eliminates oxidation of the melt during the melting and casting of the alloy and furthermore the presence of germanium markedly improves the castability of the alloy. In addition, the silver-copper alloys containing germanium, exhibit an improved resistance to tarnishing in an oral environment. These beneficial results due to germanium are obtained with little or no loss of the excellent fabricating characteristic of silver-copper alloys, when the amount of germanium does not exceed ten percent.

Thus, in accordance with the present invention a base alloy of silver-copper-germanium is provided consisting essentially of, by weight, 40 to 85% silver, 15 to 60% copper and 0.1 to 10% germanium, the base alloy of silver-copper-germanium optionally being replaced up to 15% by weight of tin and up to 10% by weight of at least one of the precious metals consisting of gold, palladium and platinum.

The beneficial effects of germanium additions to the silver-copper alloys are noticeable even in concentrations as low as 0.1% by weight; however the preferred amount of germanium which is present in the alloy is in the range of 0.5% to 2% by weight of alloys which are rich in silver and up to 10% by weight of germanium for alloys which are rich in copper. The addition of the germanium does not significantly affect toughness nor the working ability of the alloy. One of the main beneficial effects imparted to silver-copper alloys by the addition of germanium is that virtual elimination of oxidation of the alloy is obtained during melting and casting. The protection against oxidation of copper in the alloy results from the preferred oxidation of germanium and the simultaneous sublimation of the germanium oxide (GeO) as it forms. At approximately 710°C, solid germanium oxide transforms directly to the gaseous state at one atmosphere pressure, the pressure vapour increasing exponentially with temperature. Eutectic or near-eutectic silver-copper alloys which would correspond to approximately 72 parts of silver to 28 parts copper by weight, melt at a temperature of approximately 780°C. Any oxygen penetrating the alloy melt containing germanium is immediately and vigorously expelled as gaseous germanium oxide at a pressure considerably exceeding one atmosphere. Furthermore, as a result of the sublimation process, a protective blanket of gaseous germanium oxide is formed which prevents or significantly decreases the amount of atmospheric oxygen from reaching the surface of the melt. The result is a virtually oxide-free casting when germanium is present which is in direct contrast to the black oxide surface that invariably develops during the melting and casting of silver-copper alloys which contain no germanium.

The excellent casting ability of the silver-copper-germanium alloys of the present invention is believed due to the virtual absence of any oxide films on the melt surface and also due to the high surface tension as indicated by the tendency of the alloy melt to ball or spherodize. The high surface tension of the alloy melt is associated with the vaporization of the germanium oxide at the melt-air interface. In general, an increase in surface tension of a melt results in a corresponding decrease in the tendency of the melt to wet surfaces which improves flow and thereby improves the casting ability of the alloy.

The hardness of the base alloy of silver-copper-germanium composition of the present invention, in particular the preferred alloy in which the silver-copper weight ratio corresponds to the eutectic or near eutectic composition, is directly related to th finen ss of the microstructure of an all y which may be varied from a relatively coarse to an extremely fine lamellar-like structure by increasing the solidification rate of the alloy casting. I have found that for rapid solidification rates and correspondingly

Alloy	Composition Weight %		Hardness Vickers	Colour
Y-10	Silver	71.1	195	White Gold
	Copper	27.6		
	Germanium	1.3		
		100.0		
Y-15	Silver	67.7	170	White Gold
	Copper	26.3		
	Gold	4.8		
	Germanium	1.2		
		100.0		
Y-14	Silver	61.9	240	Silver
	Copper	24.1		
	Tin	12.3		
	Germanium	1.7		
		100.0		
Y-25	Silver	63.9	145	White Gold
	Copper	24.9		
	Gold	9.9		
	Germanium	1.3		
		100.0		
Y-20	Silver	67.6	130	White Gold
	Copper	26.2		
	Palladium	5.0		
	Germanium	1.2		
		100.0		
Y-18	Silver	64.7	185	Light Gold
	Copper	25.2		
	Tin	6.2		
	Gold	2.4		
	Germanium	1.5		
		100.0		

In preparing the base alloy of silver-copper-germanium, the germanium may be incorporated into the alloy by one of several methods. It may be added to the alloy melt directly in an essentially pure state or it may be added in the form of an eutectic silver-germanium master alloy containing about 19% germanium by weight. The finished base alloys may be provided in several forms, as for example, rods, sheet, strip, castings, shot, powder or compressed powder tablets. In the powder form, the germanium may be incorporated into the alloy prior to the powdering stage, or it may be admixed as a constituent powder of pure germanium or of a germanium-base alloy into the alloy powders constituting the remaining alloying components.

While the invention has been described with reference to certain specific examples and compositions, it is not necessarily confined to the details as set forth and this application is intended to cover modifications or changes as may come within the scope of the following claims.

Claims

1. A base alloy of silver-copper-germanium consisting essentially of 40 to 85% by weight silver, 15 to 60% by weight copper and 0.1 to 10% by weight germanium.

2. An alloy according to claim 1 consisting essentially of 70 to 72% by weight silver, 26 to 28% by weight copper and 0.5 to 2% by weight germanium.

3. A base alloy of silver-copper-germanium consisting essentially of 40 to 85% by weight silver, 15 to 60% by weight copper and 0.1 to 10% by weight germanium, said base alloy being replaced by up to 15% by weight tin.

4. An alloy according to claim 3 consisting essentially of 60 to 66% by weight silver, 22 t 27% by weight copper, 0.5 to 2% by weight germanium, and 10 to 15% by weight tin.

5. A base alloy f silver-copper germanium consisting essentially of 40 to 85% by w ight silver, 15 to 60% by weight copper, 0.1 to 10% by w ight germanium, said base alloy of silver-copper-germanium being replaced by up to 10% by weight of at least one precious metal selected from the group consisting of gold, palladium and platinum.

6. An alloy according to claim 5 consisting essentially of 62 to 70% by w ight silv r, 24 to 27% by weight copper, 0.5 to 2% by weight germanium and up to 10% by weight gold.

7. A base alloy of silver-copper-germanium consisting ssentially of 40 to 85% by w ight silver, 15 to 60% by weight copper, 0.1 to 10% by weight germanium, said base alloy being replaced by up to 15% by weight tin and by up to 10% by weight of at least one precious metal selected from the group consisting of gold, palladium and platinum.

8. An alloy according to claim 7 consisting essentially of 55 to 65% by weight silver, 20 to 25% by weight copper, 5 to 15% by weight tin, 3 to 7% by weight gold, and 0.5 to 2% by weight germanium.

9. A base alloy of silver-copper-germanium substantially as herein described.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.